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AN AUTOMATED GAS CHROMATOGRAPHIC SYSTEM FOR PESTICIDE RESIDUE ANALYSIS

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Gas chromatograms of pesticides and phthalate esters obtained by an automatic injection system are analyzed by a computerized gas chromatographic data system. The system described provides for simultaneous injection onto two independent columns equipped with individual detectors. The gas chromatographic output is processed by the computer into a report for each column listing the names and concentrations for compounds of interest. The system has sufficient reliability to allow detection of chlorinated pesticides at the picogram level and organophosphorous pesticides and phthalates at the nanogram level. This system is readily incorporated into currently accepted methods for pesticide residue analysis. Once the system is calibrated, 42 samples can be analyzed for 45 parameters without operator intervention.

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BRIEF

Qualitative and quantitative determination of 43 pesticide and 2 phthalates parameters is achieved automatically. Relative standard deviations range from 0.6 for the isopropyl ester of 2,4-D to 16 for o,p'-DDD.

ABSTRACT

Gas chromatograms of pesticides and phthalate esters obtained by an automatic injection system are analyzed by a computerized gas chromatographic data system. The system described provides for simultaneous injection onto two independent columns equipped with individual detectors. The gas chromatographic output is processed by the computer into a report for each column listing the names and concentrations for compounds of interest. The system has sufficient reliability to allow detection of chlorinated pesticides at the picogram level and organophosphorous pesticides and phthalates at the nanogram level. This system is readily incorporated into currently accepted methods for pesticide residue analysis. Once the system is calibrated, 42 samples can be analyzed for 45 parameters without operator intervention.

The large number and quantities of pesticides (1) in wide spread use (2,3) has aroused public concern over any unintended effects these chemicals may have on human health (4). Probable carcinogenic activity at low concentrations (4 - 11) has led to suspension orders for Aldrin and Dieldrin (12), cancellation of DDT usage (13) and intent to cancel notices for Chlordane and Heptachlor (14). This list will grow as the toxic effects of greater numbers of chemical compounds are investigated. Since time and expense necessary for clinical testing are very high (15), the effects of the majority of pesticides on man has not been firmly established (4). Thus from a practical standpoint, a knowledge of the pesticides widely distributed in the environment would be useful to more efficiently assess the threat of pesticides to human health.

An effective monitoring program to measure the concentration of each critical pesticide at enough stations to give a resonable estimate of actual conditions in the total environment requires a very high sample throughput. Usually, personnel resources are not available to perform the required numbers of analyses. In order to use available man power more effectively, semi-automation of pesticide analysis has been developed.

Many methods for the analysis of pesticides in the environment can be found in the literature (16 - 18). For water, sediment, biological and some air samples, they include extraction into a suitable solvent, elimination of non pesticide interferences and separation into three classes via florisil and silica gel column chromatography. Each chromatographic fraction is then analyzed with gas-liquid chromatographic procedures. We wish to report here the incorporation of automation into methods recommended by EPA (16-18) for pesticide residue analysis. Any of several commercially available "mini computers" interfaced to three gas chromatographic detectors may be used. Automated injection systems for gas chromatographs provide reliable alternatives to manual injection.

The data reduction system tentatively identifies components by comparing retention times (relative to an interal standard). Concentrations for components of interest are calculated using data from standard solutions, detector sensitivity and sample dilution factors. Above all, this frees the chemist while up to 42 samples (42 hours) are injected, chromatographed and analyzed.

EXPERIMENTAL

Apparatus. A Perkin-Elmer Model 3920 Gas Chromatograph equipped with a single inlet to dual column splitter, dual Ni^{63} electron capture detectors and associated electronics and dual 6 ft. x 6mm o.d. glass columns packed with: (a) 1.5% OV-17/1.95% OV-210 and (b) 4% SE-30/6% OV-210 both on 100/120 mesh Chrom Q was employed for chlorinated hydrocarbon pesticide and phthalate ester analysis. Operating conditions were: injector temperature 250°C, column temperature 210°C, transfer unit temperature 250°C, detector temperature 300°C, 5% methane: 95% argon carrier, with a flow rate for column (a) 48 ml/min and column (b) 53 ml/min.

A Perkin Elmer (Model 900) gas chromatograph equipped with a flame photometric detector was used for analysis of phosphorous containing compounds. A 6 ft. x 6mm o.d. glass column packed with 4% SE-30/6% OV-210 on 100/120 mesh Gas Chrom Q was used for original analysis and a 6 ft. x 6mm o.d. column packed with 1.5% OV-17/1.95% OV-210 on 100/120 mesh Gas Chrom Q was used for confirmation. Operating conditions were inlet temperature 250°C, transfer unit temperature 250°C, detector temperature 240°C, oven programmed from 200°C to 265°C at 4° per minute, nitrogen carrier, flow rate of 60 ml/min.

A Precision Sampling Corp. (Model 4200) autosampler distributed by Perkin Elmer Corp. equipped with a 42 sample tray and modified with a 0.011 in. injection needle (adjusted to 10 microliters) was employed for automated sampling.

A Perkin Elmer Model PEP-I Data System programmed for "Stored Method" type analysis equipped with a teletype terminal was employed for data reduction.

Reagents. Reagent grade phthalates (Fisher) were used without further purification. Pesticide standards were obtained from U.S. EPA, Research Triangle Park, North Carolina (analytical grade). Stock solutions were prepared in pesticide grade (Burdick & Jackson) n-hexane. The compounds chosen for the standard mixtures are based on elution patterns from accepted chromatographic cleanup procedures (17-19).

Procedure. Preparation of the analytical "method" includes the averaging of three injections of a solution containing compounds of interest at known concentrations with the addition of an internal standard. Preparation of the system for analyses includes monitoring background noise and acquisition of data files for compounds of interest. The system is first directed to monitor the baseline for each detector to determine values which the system should consider baseline dreft and the value proportional to area which a potential peak must surpass to be included in the output. The system then acquires data from a standard mixture which approximates the composition of the unknown sample to be run. This standard mixture is injected into the gas chromatograph and the data system stores the retention times and peak areas for each of the components. This standard injection is repeated twice. From these files an "Analytical Method" is generated.

The system is then directed into the analysis mode for calculation of relative retention times. One of the files is called up. The relative retention time chosen for the reference compound (usually 1.000) is entered. The lower and upper limits in minutes in which the peak selected is entered. The stability of the system permits these limits to be ± 0.1 minutes. The system then calculates the retention times of each component relative to the internal standard.

The system is then directed to the calibration mode to compute response factors for the components of the previously injected standard. The peak file called up for calibration is entered followed by a number to designate the "Method". The concentration of the internal standard component is entered followed by the threshold values the system calculated earlier plus the limits and relative retention time for the internal standard. The time which the system is to begin collecting (to exclude the solvent peak) and the maximum time the system is to acquire data is entered. The relative retention time and name for each component is then entered.

The concentration units are selected by the operator (in this case nanograms per sample). The system then calculates response factors with the response factor for the internal standard defined as 1.000. The system is then directed to average the files from the second and third injections of the standard solution with that used to generate the method. This procedure requires no knowledge of computer programming or maintenance and is described elsewhere in detail (19).

The automatic sampler is set for the time between injections (greater than the data acquisition time) at the sampling controller module. When the automatic sampler is actuated it advances to the first sample, injects a 10 microliter aliquot, and simultaneously activates the data system. When the data acquisition time as chosen by the operator is reached, a report is printed by the teletype, and the sampler advances to the second sample. This process is repeated till all 42 samples are injected and their contents qualitatively and quantitatively and quantitatively analyzed without operator intervention.

RESULTS AND DISCUSSION

The diversity of pesticides in the environment today necessitates the use of two chromatographic columns of different polarity to obtain a well founded pesticide identification (16, 17, 20). Chromatograms for the three classes of pesticides and phthalates listed in Table I and which are obtained in currently accepted procedures (16-18) are shown in Figures 1-3. Note that the dual column system permits simultaneous confirmation in less than an hour per sample for electron capture sensitive compounds. Dieldrin, Aldrin and Phorate are used as internal standards (see Figures 1, 2 and 3 respectively) to continuously monitor the qualitative and quantitative performance of the system. A typical report generated by the system is shown in Figure 4. The components of interest are cited by name and concentrations are reported in units selected by the operator. The analyst can then scan the reports from the dual column system to compare quantitative data based on peak areas rather than peak heights which are more subject to slight variation in chromatographic conditions (21). Typical statistical errors (as standard deviations) are displayed in Table 1. Figure 5 shows that system response vs. amount of material injected remains linear over two orders of magnitude. The number of parameters incorporated into the system is limited solely by the resolution of the chromatographic columns.

CONCLUSIONS

This automated sampling gas chromatographic data reduction system dramatically increases the number of samples and parameters analyzed with a simultaneous decrease in turn around time. Samples can be chromatographed during non-working hours with the resulting data reduced to units desired by the analyst. This system has been employed successfully to analyze drinking waters, surface waters, (22) waste waters, biological (fish) extractions and sediment extractions.

TABLE I

SYSTEM RESPONSE DATA FOR PESTICIDES ON 1.5% OV17 1.95% OV210 ON GAS CHROM Q

COMPOUND NO.	NAME	RELATIVE RETENTION TIME Ave.	Std.Dev. (n=10)	CONCENTRATION STANDARD	RELATIVE STANDARD DEVIATION FOR REPORTED VALUES (n = 15)
1.	Treflan	.470[a]	0.007	23.0	5.6
2.	Hexachloro-benzene	.523[a]	0.004	11	3.6
3.	Lindane	.691[a]	0.007	10	2.0
4.	beta BHC	.772[a]	0.006	32	2.5
5.	Heptachlor	.836[a]	0.004	10	4.0
6.	Aldrin	1.000[a]	0.005	20	3.5
7.	Zytron	1.17[a]	0.005	46	2.6
8.	Isodrin	1.27[a]	0.007	10	4.0
9.	Heptachlor epoxide	1.45[a]	0.005	20	2.5
10.	gamma Chlordane	1.60[a]	0.007	20	1.5
11.	o,p' - DDE	1.67[a]	0.007	32	2.2
12.	p,p' - DDE	2.02[a]	0.009	22	2.3
13.	o,p' - DDD	2.35[a]	0.006	22	16
14.	o,p' - DDT	2.79[a]	0.01	58	8.1
15.	pp' - DDD	3.03[a]	0.02	20	4.0
16.	pp' - DDT	3.61[a]	0.01	58	12
17.	Mirex	4.71[a]	0.02	44	4.0
18.	Methoxychlor	6.59[a]	0.02	99	8.7
19.	2,4-D isopropyl ester	0.563[a]	0.001	51	0.6
20.	Di-n-butyl Phthalate	1.10[a]	0.002	200	0.8
21.	DCPA	1.31[a]	0.002	14	2.1
22.	Endosulfan I	1.76[a]	0.003	22	1.4
23.	Dieldrin	2.11[a]	0.008	13	0.7
24.	Endrin	2.53[a]	0.003	22	1.3
25.	Chlorobenzilate	2.76[a]	0.004	94	3.3
26.	Endosulfan II	3.02	0.004	104	7.4
27.	Di-2-ethylhexyl Phthalate	5.75[a]	0.008	80	2.0
28.	Tetradifon	8.17[a]	0.01	26	11
29.	Phorate	1.000[b]	0.002	10	6
30.	Diazinon	1.24[b]	0.001	6.0	6.6
31.	Dyfonate	1.35[b]	0.001	6	6.6
32.	Ronnel	1.97[b]	0.002	14	8.5
33.	Dursban	2.28[b]	0.003	4	5
34.	Methyl Parathion	2.46[b]	0.002	8	2.5
35.	Malathion	2.59[b]	0.002	8	8.8
36.	Ethyl Parathion	3.01[b]	0.002	8	6.2
37.	DEF	3.45[b]	0.004	4	10
38.	Ethion	4.23[b]	0.004	16	5
39.	Carbophenthion	4.23[b]	0.004		
40.	Phencaptan	5.28[b]	0.005		10
41.	EPN	5.84[b]	0.005	2	

TABLE I (Con't)

COMPOUND NO.	NAME	RELATIVE RETENTION TIME Ave.	Std. Dev. (n=10)	CONCENTRATION OF STANDARD	RELATIVE STANDARD DEVIATION FOR REPORTED VALUE (n = 14)
42.	Azinphos methyl	6.23[b]	0.005	60	9.7
43.	Phosalone	6.36[b]	0.005	10	6
44.	Azinphos ethyl	6.68[b]	0.006	10	6
45.	Coumaphos	8.28[b]	0.005	60	3.8

[a] Retention time relative to aldrin at 213°C.

[b] Retention time relative to phorate; for chromatographic conditions, see experimental.

[c] n = 7

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